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APPLICATION OF NATURAL COMPLEX RAW MATERIAL IN CONTAINER GLASS PRODUCTION

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It is shown that high-silica sedimentary rock can be used as a natural raw material in energy-efficient production of colored glass containers. The phosphorus oxide present in the rock influences the viscosity and crystallization properties of the synthesized glasses. The physical and chemical properties of the glass obtained correspond to the operating properties of container glass based on conventional raw material.

Key words: natural complex mineral raw material, high-silica rock, glass batch, container glass.

Many large manufacturing plants, including glass plants, face shortages of raw material due to the exhaustion of natural conditioned raw materials, inadequacy of equipment at operating mineral enrichment plants, remoteness of raw material bases and impossibility of developing new deposits. One solution to this problem is to find sources of alternative raw materials and develop technology for using them in manufacturing. Specifically, silica-containing rocks which are common in the Russian Federation can be used in a number of cases to replace quartz sand [1, 2]. The adoption of this raw material in glassmaking makes it possible to reduce production costs by lowering the cost of glass batch and sometimes by intensifying glass production.

In the present work the possibility and prospects for replacing in glass production the conventional by unconventional raw materials are demonstrated for the example of high-silica rock (HSR) of sedimentary origin.

The chemical composition of rock consists mainly of silica and calcium-containing compounds (Table 1), which is a prerequisite for partial or complete replacement of quartz sand and calcium-containing raw material (dolomite, chalk, limestone) by HSR in the recipe for glass batch.

The oxides of alkali elements, magnesium and aluminum, which are present in small quantities in rock, are harmless impurities in glassmaking and do not limit the glassmaking process, but they must be taken into account in figuring the batch. Iron oxide is a strong colorant and at the content indicated precludes the use of rock for obtaining colorless glass. However, in the manufacture of colored glass, for example, container glass, its presence in the raw material is desirable from the standpoint of conservation of additives which are introduced in order to obtain a prescribed color tone of the glass.

The polymineral composition of rock is represented by the aggregate of dominating silica-containing phases — α-quartz, cristobalite and tridimite as well as calcium-containing phases such as gypsum (calcium sulfate dehydrate), calcite (calcium carbonate) and hydroxyapatite (apatite-like calcium hydrophosphate) (Fig. 1). Of the carbonate minerals magnesite and dolomite are possible in very small quantities. Alkaline aluminum silicates from the feldspar group — microcline and orthoclase — are found in small quantities. A halo at small angles 2θ attests to the presence of an amorphous phase. A silica matrix with individual inclusions of

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TABLE 1. Chemical Composition of High-Silica Rock (HSR)*

Component	SiO_2	Al_2O_3	P_2O_5	CaO	MgO	SrO	Na_2O	K_2O	Fe_2O_3	TiO_2	SO_3
Content, wt.%	84.90	1.1	2.49	8.69	0.83	0.03	0.85	0.13	0.54	0.06	0.38

* According to elemental analysis in terms of the oxide composition adjusted to 100%.

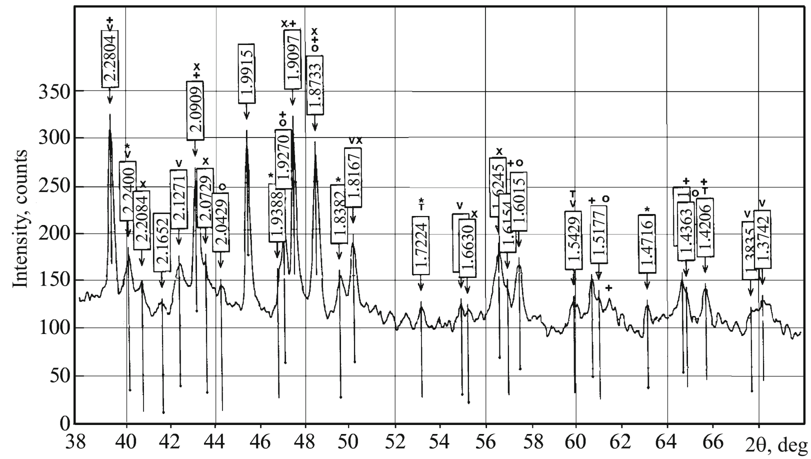

Fig. 1. X-ray diffraction pattern of high-silica HSR rock: **v**) α-quartz; **т**) tridimite; o) β-cristobalite; +) calcite; x) gypsum; ∗) hydroxyapatite.

carbonate, sulfate and phosphate compounds of calcium can be seen in photomicrographs of polished sections of lumpy rock (Fig. 2).

In summary, in terms of the mineralogical composition the rock is distinguished from conventional silica raw material used in the glass industry by the presence of, together with crystalline quartz, polymorphous modifications of silica — tridimite and cristobalite as well as water and water-free calcium-containing minerals and an amorphous phase. On the basis of theoretical considerations these factors can be expected to have a positive effect on the glassmaking process.

Phosphorus oxide in the form of calcium phosphate compounds can have a definite effect on glassmaking and the properties of glass. The scientific and technical literature indicates that additions of P_2O_5 are used in the production of sheet glass [3, 4] and improve the technological properties and performance of container glass when small amounts of phosphorus oxide are introduced [5 – 7]. Nonetheless, a high content of phosphorus oxide in glass can have an adverse effect manifesting in separation by liquation, to which many phosphorus-containing glasses are prone, as well as crystallization of glass during formation.

Several series of glasses were synthesized in order to determine the possibility and particularities of melting batch based on unconventional raw materials under laboratory conditions. The chemical compositions of the glasses were picked on the basis of the specifications in GOST R 52022–2003 [8] and practical experience in the production of colored container glass by Russian enterprises. Silicon oxide was introduced into the batch used to make the experimental glass (designated by the letter P) by means of feldspar of comminuted HSR rock. The comminuted HSR rock is a free-flowing, fine, white powder, which is not prone to strong dust generation or clumping, with two predominating fractions: average particle size smaller than 5 μm and 10 – 15 μm. Quartz sand was not present in the recipe used for these batches; conventional glass raw materials — dolomite, chalk, soda and sodium sulfate — were used to charge the composition with other components. Standard glasses with similar compositions (designated by the letter K) based on quartz sand and other convention raw materials used in glass production in Russia were also synthesized for comparative studies.

The glasses were made in 10 ml corundum crucibles at temperatures 1400 – 1500°C in a laboratory electric furnace with silicon carbide heaters and automatic temperature regulation and in 500 ml fireclay crucibles in a crucible furnace heated by gas burners.

A visual assessment of the producibility of the experimental glasses shows that all batches are prone toward glass formation at temperature 1450 – 1500°C (Fig. 3). Glass of satisfactory quality with no incomplete fusion, good fining,

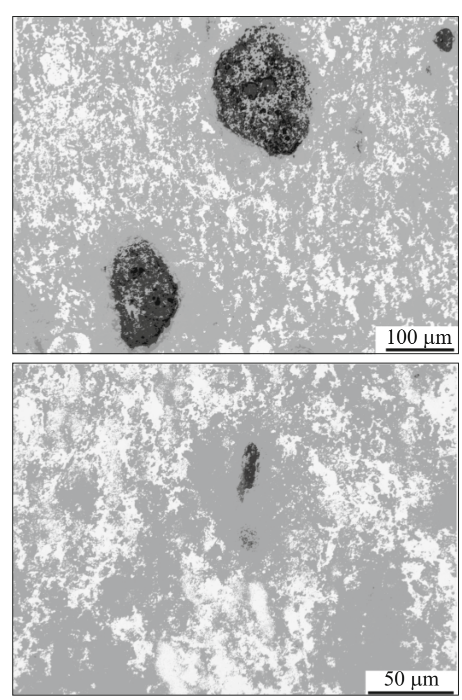

Fig. 2. Structure of lumpy high-silica rock HSR (polished sections, optical microscopy).

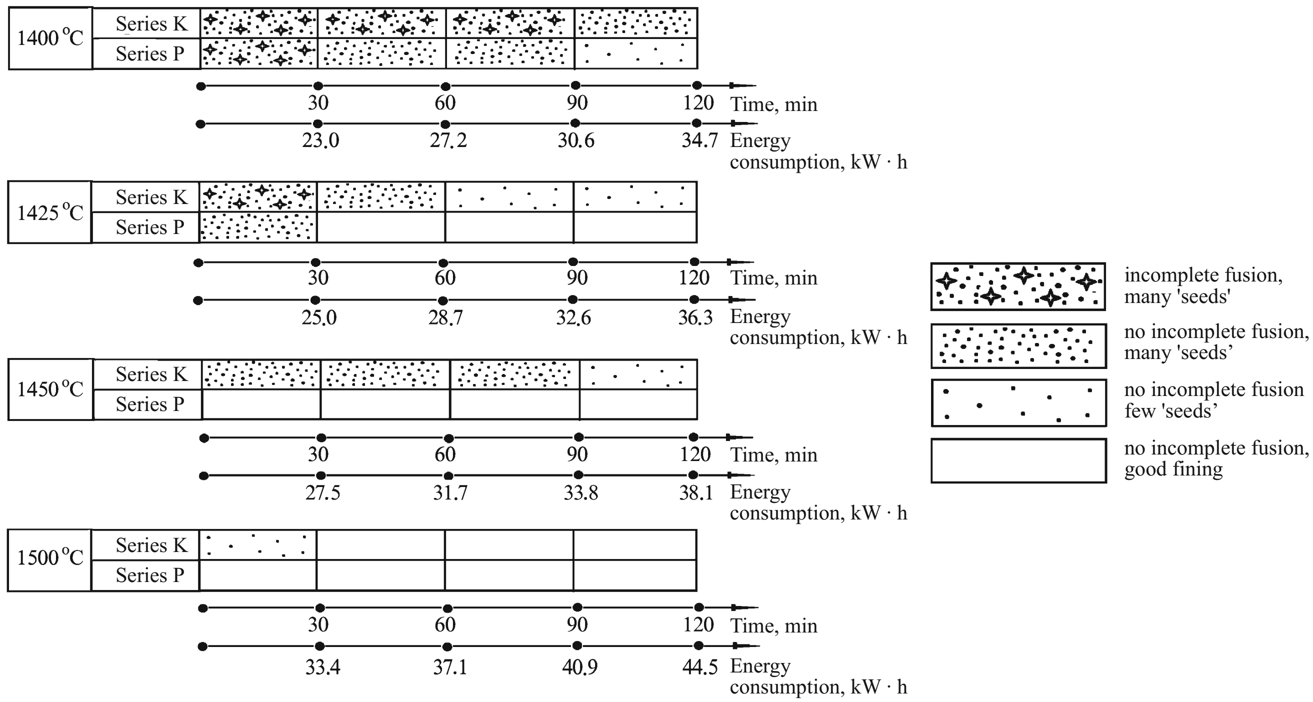

Fig. 3. Visual assessment of glasses with different temperature-time production regimes.

no indications of crystallization and a weak color tone was obtained under the optimal glassmaking conditions. No interaction of the molten glass with the crucible material (corundum, fireclay) is observed.

The experiments on glass synthesis in different temperature-time regimes with the energy consumption being continually recorded demonstrated the intensifying effect of HSR rock on the glassmaking process — high-quality fining of the molten glass with no incomplete fusion is obtained with unconventional batch at low temperature and shorter soaking of the melt as compared with conventional batch. For example, well fused and fined series P glass was obtained under laboratory conditions at 1425°C with 60 min soaking (energy consumption 28.7 kW · h), while to obtain high-quality series K melts under the same conditions the temperature must be at least 1500°C (energy consumption 37.1 kW · h) (see Fig. 3). In summary, when using unconventional batch the energy consumption for glassmaking is at least 20% lower.

These conclusions support the results of a comparative x-ray phase analysis of batches after heat-treatment at different temperatures. For example, in all batches α-quartz and cristobalite are recorded as the final crystalline phases after high-temperature treatment, but their content in the batches based on HSR is much lower than in batches based on conventional raw material (Fig. 4). The results obtained give a basis for supposing that the high-silica rock is more reactive than quartz sand, which results in intense silicate formation at early stages of glassmaking and promotes more rapid dissolution of the crystalline phases in the glass melt formed.

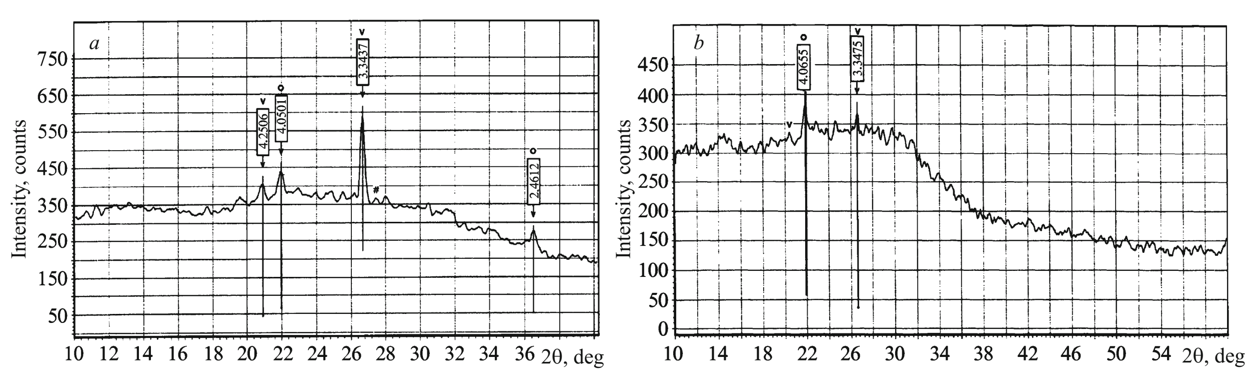

Fig. 4. X-ray diffraction patterns of glass batches heat-treated at 1200°C: *a*) series K; *b*) series P; crystalline phases: v) α-quartz; o) β-cristobalite.

TABLE 2. Characteristic Crystallization Temperatures and Parameters of Glasses

Glass series	Characteristic temperature, °C			CLTE, 10^{-7} K^{-1}	Temperature of exoeffects, °C		
	dilatometric		DSC				
	t_g	$t_{o.d}$	t_g		$t_{o.d}$	t_I	t_{II}
K	550	598	566	90	840	906	989
P	570	620	600	88	760	877	941

To develop technology for making glass and forming glasses based on unconventional raw materials it is necessary to determine the viscosity and crystallization properties of the glasses. A comparative assessment of these properties of experimental and standard glasses was made by means of dilatometry and differential scanning calorimetry (DSC) according the characteristic temperatures and the temperatures of exothermal effects due to crystallization processes occurring as glass is heated (Table 2, Fig. 5). In the process the glassmaking temperature t_g, the temperature of the onset of deformation $t_{o.d}$ and others were determined.

The results obtained attest that on the whole the viscosity parameters of the synthesized glasses fall in the range coinciding with the viscosity range of commercial sodium-calcium-silicate container glass. Nonetheless, the low-temperature viscosity of the experimental glasses is somewhat higher than that of standard glass. This behavior is observed for the glass formation temperature t_g and the deformation onset temperature $t_{o.d}$ irrespective of the method used to measure them and attests to a more highly polymerized strong structure of the glass based on unconventional batch. This result is also confirmed by the somewhat lower value of the CLTE of the series-P glass. A likely reason for the observed phenomenon is the presence in HSR rock of phosphorus oxide, which the data in [7] show to promote the formation of more high-polymerized silicon-oxygen structure of glass as a result of the transition of part of the modifier ions into an ionogenic phosphorus-containing phase forming as a result of the separation of the glass by liquation in the presence of P_2O_5.

It is evident that the liquation structure of phosphorus-containing experimental glass based on HSR also makes the glass more prone toward crystallization. Exothermal effects attesting to crystallization processes are observed on all DSC curves of all glasses at high temperatures (see Fig. 5, Table 2). It is evident that the crystallization of the series P glass starts at lower temperature and proceeds in a wider temperature range compared with the series K glass, i.e., the experimental glass is characterized by high crystallizability. The higher proneness of glass melt toward crystallization has an adverse effect on the process of formation of glass articles and results in the appearance of defects in the form of solid crystalline inclusions or crystallized surface layers in the glass. However, at the high speeds of operation of modern glass-forming machines the risk of crystallization of glass

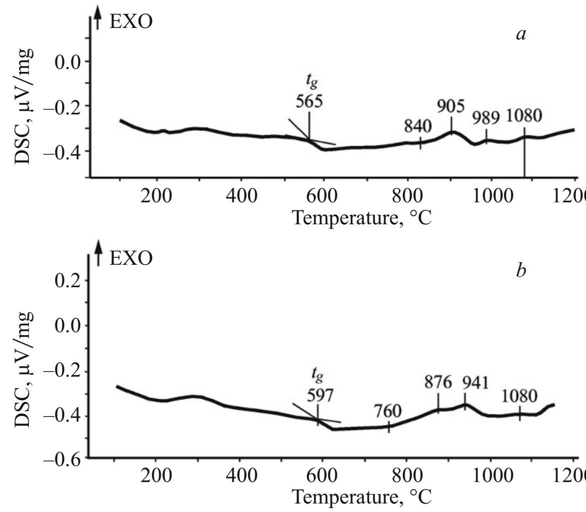

Fig. 5. DSC curves for glasses based on conventional raw materials (K glass – *a*) and on high-silica rock HSR (P glass – *b*).

during the formation is greatly reduced, so that the question of safe (from the standpoint of crystallization) production of glass articles must be solve at the time when the process parameters are worked out for the glass article production line.

The physical and chemical properties of the glasses were measured by standard procedures for samples of satisfactory quality. It was determined that according to the density, linear thermal expansion coefficient, microhardness and chemical stability the experimental glasses correspond to similar compositions of glass made using conventional raw materials. The spectral characteristics of the experimental glass are distinguished by low light transmission and light-green color tone. The absorption bands of iron ions with degrees of oxidation III and II are present in the spectral curves; this is due to the comparatively high content of iron oxide in the HSR rock used.

In summary, the results of this work attest that high-silica sedimentary rock can be used as silica- and calcium-containing raw material in the production of colored glass containers. The glass melt obtained on the basis of this raw material with the corresponding temperature-time regimes of glassmaking forms a high-quality molten glass without defects, which permits the formation of articles by methods ordinarily used in glass technology. The physical and chemical

properties of the experimental glasses correspond to those of container glass based on conventional raw materials.

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